USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 505
DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-AES

Revision 9
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1 SCOPE AND APPLICABILITY

This SOP provides procedures for the determination of dissolved and total recoverable elements by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) in environmental samples for use in the USEPA Region 9 Laboratory, Richmond, CA. These procedures are applicable to water samples only. This SOP is based on EPA Method 200.7, Rev. 4.4, *Determination of Trace Elements in Waters and Wastes by ICP-AES*, May 1994. Deviations from the reference method are described in Appendix A. Analytes and quantitation limits (QLs) are listed in Appendix B.

Water samples with turbidity > 1 NTU or where silver and/or total recoverable analytes are requested must be digested following Region 9 Laboratory SOP 403 *Aqueous Sample Preparation for ICP-AES and ICP-MS* prior to analysis. Other water samples may be analyzed directly after proper filtration and/or acid-preservation.

2 METHOD SUMMARY

An aqueous sample is nebulized and the resulting aerosol is introduced to the inductively coupled plasma torch of the ICP-AES instrument where element-specific emission spectra are produced. These spectra are dispersed by a grating and their intensities are monitored at specific wavelengths by a photomultiplier tube. The resulting intensities are proportional to the concentration of the trace elements and are processed by a computer system.

Water samples for total recoverable analytes, silver analysis, or having turbidity > 1 NTU are acid digested prior to analysis. However, dissolved elements are analyzed by "direct analysis" after filtration and acid preservation of aqueous samples. Drinking water samples are also analyzed by "direct analysis" without acid digestion if the samples have been properly acid-preserved and have turbidity of < 1 NTU.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

CRL - This is a LIMS acronym for contract reporting limit. It is a LIMS QC sample type and is equivalent to the QLS.

Optical Alignment Solution – A solution of manganese used to align the optical paths of the ICP-AES instrument.

Spectral Interference Check (SIC) Solution – A solution of selected method analytes of

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higher concentration which is used to evaluate the procedural routine for correcting known inter-element spectral interferences with respect to a defined set of method criteria.

Total Recoverable Analyte Concentration – The concentration of an analyte in an unfiltered aqueous sample after preparation by acid digestion.

4 SAFETY & HEALTH

All laboratory personnel must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument that are not intended for access by the instrument operator. Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for

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pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure.* Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable

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Waste Stream Description	Waste Label	Hazard Properties
ICP-AES instrument liquid waste (nitric acid, hydrochloric acid, trace metals)	Hazardous Waste	Corrosive, Toxic

NOTE: Arsenic (50,000 mg/kg), beryllium (7500 mg/kg), cadmium (10,000 mg/kg), lead (1300mg/kg dry), selenium (10,000 mg/kg), and thallium (70,000 mg/kg) are listed as extremely hazardous wastes at concentrations greater than or equal to those indicated. As such, any sample, sample digestate, or sample extract/leachate with a concentration exceeding these levels must be handled as an extremely hazardous waste. Should one or more of these concentrations be determined, notify the LaSHEM (or designee).

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned polyethylene containers. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. A 500-mL sample volume should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form. If discrepancies are noted, inform the sample custodian.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to "active out" and the location to the appropriate room number. At the end of the day, return sample containers to the "Home" locations. Update the LIMS database using the "return to home location" feature and update container disposition to "available in". Verify that your initials are recorded whenever you update the LIMS custody information.

Sample digestates for metals analysis are received from the digestion lab personnel and custody is transferred to the metals analyst. The metals analyst acknowledges the receipt of the sample digestates by signing the appropriate section of the completed LIMS bench sheet.

5.3 Preservation Verification

5.3.1 Drinking Water Samples – Samples are preserved by acidifying with dilute nitric acid to pH < 2 (normally, 3 mL of dilute nitric acid per liter of sample is

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sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH < 2 just prior to withdrawing an aliquot for turbidity measurement.

5.3.2 Dissolved Analyte Samples – The samples must be filtered through a 0.45-µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Glass or plastic filtering apparatus are recommended to avoid contamination. The laboratory must perform filtration immediately if the step was not performed in the field. Acidify the filtrate with dilute (1:1) nitric acid immediately following filtration to pH < 2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient).

5.3.3 Aqueous Total Recoverable Analyte Samples – Samples are preserved by acidifying with dilute nitric acid to pH < 2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH < 2 just prior to withdrawing an aliquot for digestion. If the pH of the sample is > 2, more acid must be added and the sample held for sixteen hours until verified to be pH < 2.

5.4 Sample Storage

Samples must be stored at > 0 and ≤ 6° C. Retain samples for 60 days after the final analytical report is sent to the data user.

5.5 Holding Time

Samples must be analyzed within six months from collection.

5.6 Sample Extracts/Leachates and Digestates

Retain sample extracts/leachates and digestates for 60 days after the final analytical report is sent to the data user.

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6 INTERFERENCES

6.1 Spectral Interferences

Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or the unresolved overlap of molecular band spectra.

Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak. The location(s) used for the routine measurements must be free of off-line spectral interferences (inter-element or molecular) or adequately corrected to reflect the same change in background intensity that occurs at the wavelength peak.

Spectral overlaps can be compensated for by equations that correct for the inter-element contributions, which involve measuring the interfering elements. When present and uncorrected, these interferences will produce false-positive or false negative results and be reported as analyte concentrations.

When inter-element corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions. Inter-element corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Inter-element corrections will also vary depending upon the choice of background correction points. Selecting a point where an interfering emission line may appear should be avoided when practical. Inter-element corrections that constitute a major portion of an emission signal may not yield accurate data. It should not be forgotten that some samples contain uncommon elements that could contribute spectral interferences.

The interference effects must be evaluated for each individual instrument. Intensities will vary not only with the optical resolution but also with the operating conditions (such as power, viewing height, and argon flow). The EPA Region 9 Laboratory has determined and documented for each wavelength the effect from the known interferences given in Table 1 of Appendix D, and utilizes a computer routine for their automatic correction on all analysis. To determine the appropriate location for the off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line inter-element spectral interference or a computer routine must be used for their automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference

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effect from all method analytes and provide for their automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 50 mg/L to 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit.

When inter-element corrections are **not** used, the ongoing SIC solutions (Section 7.3.7) must be analyzed to verify the absence of inter-element spectral interference. When the interference accounts for 10% or more of the analyte concentration, another approved test procedure must be used to complete the analysis. Users should be aware that, depending upon the instrumental resolution, alternate wavelengths with adequate sensitivity and freedom from interference might not be available for all matrices. In these circumstances, the analyte must be determined using another approved test procedure.

6.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples that contain high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by such means as high solids nebulizer, diluting the sample, and using a peristaltic pump. Another problem that can occur is salt buildup at the tip of the nebulizer, which affects the aerosol rate and causes instrument drift. This problem can be controlled by a high solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample.

6.3 Chemical Interferences

Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP-AES technique. If observed, they can be minimized by careful selection of operating conditions (such as incident power and observation height), buffering the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

6.4 Memory Interferences

Memory interferences are related to sample transport and result when there is carryover from one sample to the next. Sample carryover can result from sample deposition on the uptake tubing to the nebulizer, and from incomplete rinsing of the sample solution from the plasma torch and the spray chamber between samples. These

memory effects are dependent upon both the analyte being measured and sample matrix and are minimized through the use of extended rinse times.

6.5 Chemical Contamination

When determining boron in aqueous samples, only plastic, PTFE, or quartz labware should be used from time of collection to completion of analysis. When possible, borosilicate glass should be avoided to prevent contamination of boron.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives and isolated from other laboratory glassware. Refer to EPA Region 9 Laboratory SOP 130 *Glassware Cleaning Procedures* for specific instructions.

7.1 Instruments and Equipment

- Perkin Elmer Optima 5300 DV Inductively Coupled Plasma – Optical Emission Spectrometer
- Perkin Elmer AS-93plus Auto-sampler

7.2 Reagents

Reagents may contain impurities that might affect analytical data. Only materials that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use.

Record all chemical and reagent preparations in the LIMS.

- Reagent Water – All references to reagent water in this SOP refer to laboratory deionized water as described in EPA Region 9 Laboratory SOP 825 *Deionized Water Monitoring*.

- Hydrochloric Acid (HCl), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed).

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- Nitric Acid (HNO_3), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed).

- Argon gas supply, high-purity grade, 99.99%.

7.2.1 Hydrochloric Acid, dilute (1:1) – Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.2 Nitric Acid, dilute (1:1) – Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1L.

7.3 Standards

Record all standards and standard preparations in the LIMS.

7.3.1 Stock Standards

Stock standard solutions are available from a commercial suppliers such as Spex CertiPrep, Ultra Scientific, or Inorganic Ventures. Individual (1,000 mg/L or 10,000 mg/L) and multi-element solutions containing elements listed in Appendix B are typically used.

7.3.2 Initial Calibration Standards

Prepare initial calibration standard solutions to contain final concentrations listed in Table 2 of Appendix D. Prepare each calibration solution using an appropriate amount of the calibration stock standard (Section 7.3.1) and dilute to 200 mL with 2% nitric acid / 2% hydrochloric acid solution.

7.3.3 ICV/CCV/SCV Standard

The ICV and CCV standards are identical and only differentiated by their place within the analytical sequence. The ICV standard also serves as the SCV. This standard is obtained from an outside source different from the initial calibration stock standards. This standard is available from Spex and consists of solution LPC Standard 1, P/N LPC-1-500 (containing Al, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Sb, Se, SiO_2, Sn, Ag, Na, Sr, Tl, V, and Zn). Titanium and cerium are added from separate 1,000 mg/L individual stock standards. Prepare the ICV/CCV/SCV standard by adding 50 mL of the LPC Standard 1 and 1 mL each of the Ti and Ce 1,000 mg/L stock standards, dilute to 500 mL with 2% nitric acid / 2% hydrochloric acid solution.

The ICV/CCV/SCV concentrations are listed in Table 3 of Appendix D. Similar mixes from other vendors can be substituted as needed.

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NOTE: ICV standard for lithium is prepared from a separate individual standard and run in a separate method.

7.3.4 CB

Dilute concentrated nitric acid and hydrochloric acid with reagent water to obtain a 2% nitric acid / 2% hydrochloric acid solution.

7.3.5 MB

Prepare the MB using reagent water plus all of the reagents used in processing the samples. The MB is taken through the entire preparation and analytical sequence.

7.3.6 LCS and MS/MSD

Use commercially available spiking solutions (e.g. Inorganic Ventures Laboratory Fortifying Stock Solutions WW-LFS-1 containing Al, As, Ba, Be, B, Cd, Ca, Ce, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, K, Se, Ag, Na, Sr, Tl, V, and Zn;and WW-LFS-2 containing Sb, Mo, SiO_2, Sn, and Ti). Prepare the LCS by spiking 0.5 mL each of the two spiking solutions into 50 mL reagent water and adding the appropriate acids. Prepare the MS and MSD by spiking 0.5 mL each of the two spiking solutions into 50 mL of the designated MS and MSD samples and adding the appropriate acids. The final concentrations for the LCS and MS/MSD are listed in Table 3 of Appendix D.

7.3.7 Spectral Interference Check (SIC) Solutions

When inter-element corrections are applied, spectral interference check (SIC) solutions containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors are needed. The SIC solutions used are 300 mg/L Ca, 200 mg/L Mg, 200 mg/L Al, 300 mg/L Fe, 50 mg/L Ba, 50 mg/L Cd, 50 mg/L Be, 50 mg/L Ce, 50 mg/L Co, 50 mg/L Cr, 50 mg/L Cu, 50 mg/L Mn, 50 mg/L Mo, 50 mg/L Ni, 50 mg/L Ti, and 50 mg/L V. Higher level SIC solutions or other SIC solutions may be used if high or unusual sample matrix are encountered. Prepare SIC solutions by diluting single element stock solutions in 2% nitric acid / 2% hydrochloric acid solution.

7.3.8 QLS (CRL in LIMS)

Prepare the QLS as needed from multi-element stock solutions (Section 7.3.1) in 2% nitric acid / 2% hydrochloric acid solution. The QLs are listed in Appendix B.

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7.3.9 Optical Alignment Solution

A solution of 1 mg/L manganese is needed to align the optical paths of the instrument. The solution is made by diluting 1.0 mL of 1,000 µg/mL manganese stock standard to 1,000 mL with 2% nitric acid / 2% hydrochloric acid solution.

7.3.10 Rinse Blank

Dilute concentrated nitric acid and hydrochloric acid with reagent water to obtain a 2% nitric acid / 2% hydrochloric acid solution.

7.4 Supplies

- Automatic pipettes capable of delivering volumes of 10 to 1,000 µL.
- Class A volumetric flasks, graduated cylinders, and funnels (glass and/or metal-free plastic).
- Class A volumetric pipettes.
- Metal-free disposable tips.
- Narrow-mouth storage bottles with screw closure, 125-mL to 1-L capacities.
- Syringe with 0.45-µm disk filters.
- Wash bottle with screw closure, 1,000-mL capacity.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set-up the ICP-AES following operating instructions provided by the manufacturer and discussed below. Use operating parameters provided in Appendix E as a starting point.

Ensure that all appropriate waste containers are properly connected and labeled and that the containers will not overflow.

Check the condition of the pump tubing for wear. Replace as needed. Tighten the pump tubing on the pump. Check torch for salt build up. Ignite the plasma and allow to stabilize for at least 30 minutes. During instrument warm up, observe the nebulizer and spray chamber for proper nebulization.

8.1.1 Method File Setup

Select the appropriate master method file and save it to correspond to the current date (e.g., 2007_150730 or yymmdd). Enter the results data set file

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name to also correspond to the current date (e.g., 11507301, indicating ICP instrument number (1), present date (yymmdd), and analytical run number (1)) in the automated analysis control window. Save all changes.

Set up the sample information editor table with the desired sample run. The most recent sample information editor files may be written over and resaved. Print the run list from the automated analysis control window. Place the standards and samples in the racks as indicated by the run list.

8.1.2 Alignment of the Optical Paths

Alignment is performed when the sample introduction apparatus is adjusted, such as a new torch, injector tip, or after manipulation of the spray chamber. Align the axial and radial optical paths of the instrument using the 1 mg/L manganese solution. Aspirate the alignment solution and run the alignment routine as per the manufacturer's procedure.

8.2 Calibration

8.2.1 Initial Calibration

A calibration blank (Section 7.3.4) and a calibration standard (Section 7.3.2) are used for calibration. The calibration standards are given in Table 2 of Appendix D. The calibration is automatically saved in the result data set file as they are run.

Perform an initial calibration for every analytical batch. Refer to Section 9.2.4 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze the ICV/SCV, CB, QLS, and SIC (verification) according to Section 8.3.2 immediately after analyzing the initial calibration standards. If QC criteria are not met, take corrective action as described in Sections 9.2.3 and 9.2.4 and Appendix C.

8.2.2 Continuing Calibration

Prepare the CCV and CB as described in Sections 7.3.3 and 7.3.4. Refer to Section 9.2.5 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

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Digest samples with turbidity > 1 NTU and/or where silver is requested following EPA Region 9 Laboratory SOP 403 prior to analysis.

Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices, and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason, samples are digested prior to the determination of silver. The total recoverable sample digestion procedure is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, a smaller volume of a well-mixed sample aliquot must be digested until the analysis solution contains < 0.1 mg/L silver.

8.3.1.1 Aqueous Samples, Total Recoverable Analytes

For the determination of total recoverable analytes in water, digest samples following EPA Region 9 Laboratory SOP 403 prior to analysis.

The digestion procedures used in EPA Region 9 Laboratory SOP 403 will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

The total recoverable sample digestion procedure is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains < 0.1mg/L silver.

8.3.1.2 Aqueous Samples, Dissolved Analytes

For the determination of dissolved analytes in ground and surface waters, add a 30-mL aliquot of the filtered, acid-preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

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The LCS and MS/MSD are prepared by spiking 0.3 mL each of the two spiking solutions (Section 7.3.6) into 30 mL of the designated LCS, MS, and MSD samples. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The final concentrations for the LCS and MS/MSD are listed in Table 3 of Appendix D.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in EPA Region 9 Laboratory SOP 403 prior to analysis.

8.3.1.3 Drinking Water Samples, Total Recoverable Analytes, Direct Analysis

Drinking water samples with turbidity < 1 NTU must be acidified and analyzed directly without digestion. Add a 30-mL aliquot of the unfiltered, acid-preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

The LCS and MS/MSD are prepared by spiking 0.3 mL each of the two spiking solutions (Section 7.3.6) into 30 mL of the designated LCS, MS and MSD samples. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The final concentrations for the LCS and MS/MSD are listed in Table 3 of Appendix D.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in EPA Region 9 Laboratory SOP 403 prior to analysis.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument run log or the LIMS sequence page, if available.

After calibration, the auto-sampler continues with the samples and QC. Load SIC solutions according to the requested analyte list. An example of a typical loading list for an analytical run sequence is listed in the table below.

Seq.	Description	Seq.	Description	Seq.	Description	Seq.	Description
1	ICV/SCV	15	Mo SIC	29	S5	43	S17
2	CB	16	Ni SIC	30	S6	44	S18

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Seq.	Description	Seq.	Description	Seq.	Description	Seq.	Description
3	QLS (CRL in LIMS)	17	Ti SIC	31	S7	45	S19
4	Ca SIC	18	V SIC	32	S8	46	S20
5	Mg SIC	19	MB	33	S9	47	MB
6	Ba SIC	20	LCS	34	S10	48	LCS
7	Al SIC	21	S1	35	S11	49	CCV
8	Cr SIC	22	S1-MS	36	S12	50	CB
9	Co SIC	23	S1-MSD	37	CCV	51	QLS (CRL in LIMS)
10	Cu SIC	24	S2	38	CB	52	S1
11	Fe SIC	25	CCV	39	S13	53	S2
12	Mn SIC	26	CB	40	S14	54	S3
13	CCV	27	S3	41	S15	55	CCV
14	CB	28	S4	42	S16	56	CB

NOTE: Be, Ce, and Cd SIC solution should be analyzed if samples contain these elements at a significant enough concentration to interfere on the analyte of interest (i.e. 1 mg/L).

Review results for QC compliance and off-scale results. Identify samples that must be re-analyzed. Samples having analytes at concentrations higher than 90% of the LDR must be diluted into range and reanalyzed. Refer to Appendix G for guidance on what elements may be reported from this analysis.

8.3.3 Analyte Identification and Quantitation

After set-up and calibration, the software reports results for the analyzed solution in the units of mg/L without inter-elemental correction. The data are then reprocessed to include inter-elemental correction when necessary.

8.3.4 Procedure to Acquire and Reprocess Data

1. Open the result data set in the Inter-Element Correction Model Builder (IEC Model Builder) set-up page. Assign the analyte limits of correction in the set limits page, generally ½ each of the corresponding QL.

2. Select the SIC samples and the interfering element.

3. Save the IEC Model Builder as 200.7IECmonth/day/year.

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4. Update the daily method from the summarize factors page of the IEC Model Builder and save as the same method name with R at the end of name to indicate that it is a reprocessed method file.

5. Print the method and summarize factor table and include with the data package.

6. Open the data reprocessing window and reprocess the result data set. Print and save in a reprocessed result data set file with the same file name as the original data set with an R at the end to indicate that it is a reprocessed data.

7. The reprocessed data includes the calibrations and IEC corrected data for all samples analyzed.

8. An IEC table from a previous run may be used to reprocess data if the appropriate SIC solutions are run to verify the IEC factors according to Section 9.2.

8.3.4.1 Aqueous Samples – Data for aqueous samples should be reported in units of µg/L using the following calculation:

$$C = M \times \frac{1000ug}{mg} \times D$$

Where

C = final reported concentration, in µg/L;
M = measured concentration reported by instrument, in mg/L;
D = Sample analysis dilution factor, to account for any dilution performed after sample preparation. For samples analyzed by direct analysis, include the factor introduced by the addition of 1:1 nitric acid.

8.3.4.2 Hardness by Calculation

Hardness is determined by calculation if samples are known to contain high concentrations of heavy metals and cannot be analyzed by titration or when requested by a client. The calculation is based on calcium and magnesium results by EPA Method 200.7.

NOTE: Calcium and magnesium must be reported from one run – if one is over calibration, both should be reported from the dilution.

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Hardness is calculated using the following equation based on Standard Method 2340B:

Hardness, mg/L $CaCO_3$ = Ca, mg/L (2.497) + Mg, mg/L (4.118)

8.3.5 Data and QC Review

Review the results of instrument QC (ICV/SCV, CB, QLS, and SIC) immediately after analysis to verify that the results are within QC limits. Refer to Section 9.2 for corrective action requirements and Appendix C for QC limits.

Review the results of batch QC (MB, LCS, MS/MSD) immediately after analysis to verify that the results are within QC limits. Refer to Section 9.3 for corrective action requirements and Appendix C for QC limits.

8.3.6 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using Data Tool. Review final results in the LIMS.

The LIMS will report two significant figures and detected results to one-half the QL. The LIMS will flag values between one-half the QL and the QL as estimated (J). The analyst must manually add a qualifier flag (C1) indicating that the reported concentration is estimated because it is less than the quantitation limit. Qualify data based on QC results and guidelines in the EPA Region 9 Laboratory QA Plan.

Archive data files to the appropriate instrument data subdirectory on the EPA Region 9 LAN.

8.4 Maintenance

Perform the following maintenance:

- Inspect pump tubing for wear daily, replace if necessary.
- Inspect spray chamber for good nebulization.
- Inspect torch and tip if starting is difficult or if unusual carry over is observed during analysis. Remove and clean as necessary.
- Clean and lubricate auto-sampler as needed.

Refer to Appendix F for preventative maintenance procedures and schedules.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 *Demonstration of Capability*.

9.2 Instrument QC

9.2.1 Linear Dynamic Range

The upper limit of the LDR must be established for each element used in quantifying results. Analyze a series of standards with concentrations spanning the range from the QL to the LDR standard concentration. The upper concentration factor can be adjusted by the analyst to account for detector characteristics or dissolved solids limitations/restrictions. From the analysis determine the maximum concentration for which the measured and true concentration agree within 10%. This concentration is typically defined as the upper limit of the LDR. Samples with analyte concentrations that are greater than 90% of the upper LDR limit must be diluted and reanalyzed. The LDR should be verified annually or whenever the analytical conditions are changed.

9.2.2 Method Detection Limit

A method detection limit must be confirmed annually and must be <½ the QL.

9.2.3 Spectral Interference Measurement and Check

The laboratory must establish and initially verify an inter-elemental spectral interference correction routine to be used during sample analysis. Criteria for determining an inter-element spectral interference is the apparent positive or negative concentration on the analyte that is outside the limits of the calibration blank for the analyte. Once established, the interferences are measured daily as needed. The test criteria and the solutions are as follows:

- For interferences from aluminum and iron, only those correction factors (positive or negative) when multiplied by 100 that exceed ±½ the QL are tested daily.

- For all other interfering elements, only those correction factors (positive or negative) when multiplied by 10 that exceed ±½ the QL are tested daily.

- If the correction routine is operating properly, the determined apparent analyte concentration from analysis of each interfering solution should fall within a specific concentration range. The range shall be the greater of either ±½ the QL or a calculated concentration range (multiply the concentration of the interfering element by the value of the correction factor being tested and dividing by 10). If the apparent analyte concentration is outside the greater of the two ranges, the correction factor should be re-determined and samples re-analyze.

- If the samples analyzed do not contain concentrations of the interfering elements at a significant concentration, daily verification is not required. A significant concentration is the concentration of interfering elements the causes a false concentration of analyte greater than ½ the QL concentration.

9.2.4 Initial Calibration

An initial calibration is performed for every analytical batch using a blank and a calibration standard for each analyte.

If an ICAL fails because of one standard mix, a fresh solution of that standard may be reanalyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration standard mix), the system must be checked so that the criteria are satisfied before any samples are analyzed.

The calibration is verified by the analysis of an ICV and CB. If the criteria for those standards are not met, take corrective action as needed before continuing with analysis, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary. The analysis may also continue but samples cannot be analyzed for the out-of-control analytes.

9.2.5 Initial and Continuing Calibration Verification

To check instrument performance and verify the accuracy and stability of the calibration, analyze an ICV and CCV standards. The ICV is analyzed immediately following initial calibration and the CCV at a frequency of one

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per 10 analytical samples and at the end of the analytical run. The recovery of analytes in the ICV and CCV are calculated as follows:

$$\%R = \frac{ICV\ /\ CCV}{S} \times 100$$

Where

$\%R$ = percent recovery
ICV/CCV = measured concentration of analyte in the ICV/CCV, mg/L
S = expected analyte concentration in the ICV/CCV, mg/L

The ICV recovery and RSD criteria are listed in Appendix C. If the %R or RSD for any analyte in the ICV falls outside of the QC criteria, the instrument must be recalibrated for at least the out-of-control analytes or analyze another second source solution containing the out-of-control analytes. If it passes, continue with analysis. Samples cannot be analyzed for the out-of-control analytes until an acceptable ICV is analyzed.

The CCV recovery criteria are listed in Appendix C. If the %R for any analyte in the CCV falls outside of the QC criteria, the instrument must be recalibrated for at least the out-of-control analytes or analyze another second source solution containing the out-of-control analytes. If it passes, continue with analysis. All samples not bracketed by acceptable CCV results must be reanalyzed.

9.2.6 Calibration Blank

The stability of the baseline must be monitored by analyzing a CB immediately after every ICV/CCV standard. If the value of the CB result is less than ½ the QL, the result is acceptable. If the value of the CB result equals or exceeds one-half the QL, the analysis may continue but samples cannot be analyzed for the out-of-control analytes. The cause of the high CB result must be determined and the problem corrected. The instrument must be recalibrated at least for the out-of-control analyte and all samples not bracketed by acceptable CB results must be reanalyzed.

9.2.7 Second Source Calibration Verification

Analyze an SCV daily to verify the calibration standards and acceptable instrument performance. The ICV serves as the SCV for this SOP.

9.2.8 Quantitation Limit Standard (CRL in LIMS)

To verify the ability to detect target analytes near the QL, a QLS must be analyzed at the beginning of the analytical run and after 40 analytical samples.

If using an auto-diluter to analyze samples, use the diluter also to analyze the QLS.

The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where
$\%R$ = percent recovery
M = measured concentration of analyte, mg/L
T = true concentration of the analyte in the QL, mg/L

If the QLS recovery does not meet the criteria in Appendix C, determine the cause, take corrective action, and reanalyze the QLS.

9.2.9 Spectral Interference Check

Analyze SIC solutions daily to measure and test inter-elemental spectral correction factors. If the SIC solutions do not meet the test criteria given in Section 9.2.3 and Appendix C, the factor must be updated before samples are analyzed for an affected analyte. If the affected samples do not contain concentrations of the interfering elements at a significant level, daily verification is not required. If the affected samples contain concentrations of analyte at less than ½ the QL, daily verification is not required. If the corrected concentration of the analyte due to spectral interference is less than 10% of the total analyte concentration, daily verification is not required.

9.3 Batch QC

9.3.1 Method Blank

Analyze one MB with each batch of 20 or fewer field samples of the same matrix. MB values ≥ ½ the QL indicate potential laboratory or reagent contamination. Use the following guidelines to determine when samples must be re-prepared, reanalyzed, and flagged as estimated:

- If the MB analyte value is ≥ ½ the QL and the sample result is less than five times the MB analyte amount, rerun the MB once to verify and if still unacceptable then the MB and all associated samples must be re-prepared and reanalyzed. If agreed to by the Chemistry Team Leader, the associated sample results can also be reported but will be qualified as estimated "J" and flagged "B" and a note placed in the Work Order memo field in LIMS.

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- If the MB analyte value is ≥ ½ the QL and the sample result is non-detected or is greater than five times the MB analyte concentration, report sample results without qualification.

9.3.2 LCS

Analyze one LCS with each batch of 20 or fewer samples of the same matrix. Recovery of analytes in the LCS is calculated as:

$$\%R = \frac{LCS}{s} \times 100$$

Where

$\%R$ = percent recovery
LCS = measured concentration of analyte in the LCS, mg/L
s = analyte concentration in the LCS, mg/L

If the recovery of the LCS does not meet the recovery criteria in Appendix C, reanalyze once to verify. If the recovery is still unacceptable, the analyte is judged to be out- of-control and the source of the problem must be identified and resolved. All samples associated with the out-of-control LCS must be re-prepared and reanalyzed. In some cases, the associated sample results can also be reported with prior approval from the Laboratory QA Officer or Technical Director. The results will be qualified as estimated "J".

9.3.3 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the effect of sample matrix on the measurement system. One set of MS/MSD samples must be prepared for every 20 or fewer field samples of the same matrix in an SDG. Homogenize the routine sample selected as the QC and spike a representative aliquot with the analytes of interest prior to any sample preparation. The spiking level must be the same as that used for the LCS.

Samples identified as field blanks cannot be used for MS/MSD sample analysis. MS/MSD recoveries are calculated as:

$$\%R = \frac{Cms - C}{s} \times 100$$

Where

$\%R$ = percent recovery

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C_{ms} = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions
C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions
s = expected spiked analyte concentration in the MS, corrected for sample preparation and any dilutions

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmsd - Cms|}{(Cmsd + Cms)/2} \times 100$$

Where
RPD = relative percent difference
C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions
C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions

If the value of C is less than four times the value of s, apply accuracy and precision criteria in Appendix C. If the value of C is greater than four times the value of s, $\%R$ is not meaningful. If the MS/MSD does not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS/MSD accuracy and precision is likely to be matrix-related. Flag any out-of-control results as estimated "J".

9.4 Method Performance

The following table summarizes method performance for the period June 1, 2014 to June 19, 2015.

Method Performance

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation	95% Confidence Interval (2σ) Lower	Upper
Aluminum	70	103	4.58	93.8	112
Antimony	52	109	4.28	100	118
Arsenic	52	109	4.25	100	117
Barium	54	106	4.42	97	115
Beryllium	52	104	4.49	94.5	112
Boron	69	102	6.38	88.7	114
Cadmium	52	104	3.59	96.9	111

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation	95% Confidence Interval (2σ) Lower	Upper
Calcium	90	108	7.2	94	123
Chromium	54	104	3.79	96.2	111
Cobalt	55	103	3.45	95.7	109
Copper	66	99.9	3.28	93.4	106
Iron	94	103	5.3	92.5	114
Lead	52	104	3.81	96.4	112
Lithium	11	107	4.06	99.3	116
Magnesium	82	103	4.64	94.1	113
Manganese	55	103	4.77	93.2	112
Molybdenum	72	103	3.17	96.5	109
Nickel	67	105	3.81	97.4	113
Potassium	67	107	3.61	99.9	114
Selenium	53	111	4.94	101	120
Silica (SiO2)	52	110	4.75	101	120
Silver	52	104	4	96	112
Sodium	82	109	6.36	96.2	122
Strontium	55	107	4.52	98	116
Thallium	52	102	4.27	93.2	110
Tin	55	101	6.33	88.7	114
Titanium	73	103	3.8	95.2	110
Vanadium	73	104	2.96	97.9	110
Zinc	67	109	4.25	101	118

The primary sources of analytical error are:

- Analytical balance
- Digestion equipment contamination
- Instrument calibration
- Interferences (See Section 6)
- Pipette calibration

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV/SCV, QLS, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the standard pdf (printed upon request).

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS or in the instrument Sequence Log. Project Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, dilution factors, and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained on the local area network or on the Lab QA SharePoint site in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on the local area network, LIMS, or the Lab QA SharePoint site for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

U.S. Environmental Protection Agency. Method 200.7, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Atomic Emission Spectrometry, Revision 4.4, EMMC Version, May 1994.

Standard Methods for the Examination of Water and Wastewater, Method 2340B, Hardness by Calculation, 20th Edition, 1998.

Perkin Elmer, Optima 5000 Series Hardware Guide.

Perkin Elmer, *AS93plus User's Guide.*

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APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP does not include mercury as an analyte. Mercury is listed as an analyte in the reference method.

2. Aqueous samples with less than 1% undissolved solids are brought to a final volume of 50 mL. This procedure does not include the sample concentration step specified in the reference method.

3. The Region 9 Laboratory does not subtract the MB results from the LCS results for LCS recovery calculation. The reference method allows MB subtraction.

4. This SOP specifies that the MB acceptance criterion is less than one-half the QL. The reference method specifies no greater than 2.2 times MDL.

5. SIC acceptance criterion of ½ the QL is being followed in this procedure.

6. The SIC solutions of thallium, silica, and tin listed in the reference method are not necessary for this instrument and are not analyzed.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the CAS number and quantitation limits.

Analyte	Chemical Abstract Services Registry Number (CASRN)	Quantitation Limit, µg/L
Aluminum (Al)	7429-90-5	100
Antimony (Sb)	7440-36-0	20
Arsenic (As)	7440-38-2	20
Barium (Ba)	7440-39-3	10
Beryllium (Be)	7440-41-7	0.5
Boron (B)	7440-42-8	100
Cadmium (Cd)	7440-43-9	5
Calcium (Ca)	7440-70-2	100
Chromium (Cr)	7440-47-3	10
Cobalt (Co)	7440-48-4	5
Copper (Cu)	7440-50-8	10
Iron (Fe)	7439-89-6	100
Lead (Pb)	7439-92-1	20
Lithium (Li)	7439-93-2	2
Magnesium (Mg)	7439-95-4	500
Manganese (Mn)	7439-96-5	5
Molybdenum (Mo)	7439-98-7	20
Nickel (Ni)	7440-02-0	10
Potassium (K)	7440-09-7	2000
Selenium (Se)	7782-49-2	20
Silica (SiO_2)	7637-86-9	500
Silver (Ag)	7440-22-4	5
Sodium (Na)	7440-23-5	500
Strontium (Sr)	7440-28-6	2
Thallium (Tl)	7440-28-0	20
Tin (Sn)	7440-31-5	100
Titanium (Ti)	7440-32-6	10
Vanadium (V)	7440-62-2	4
Zinc (Zn)	7440-66-6	10

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APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
ICV/SCV	After ICAL	95 - 105%
ICV	After ICAL	< 3% RSD
CCV	Every 10 samples and end of run	90 - 110%
CB	After each ICV/CCV	< ½ QL
QLS	After ICAL and after every 40 samples	60 - 140%
MB	Each batch of 20 or fewer samples	< ½ QL
LCS	Each batch of 20 or fewer samples	85 - 115%
MS/MSD, Accuracy	Every 20 or fewer samples in an SDG	70 - 130%
MS/MSD, Precision	Every 20 or fewer samples in an SDG	≤ 20 RPD
SIC	After ICAL, as needed per analyte	±½ QL or calculated acceptance window, whichever is greater

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APPENDIX D.
STANDARD TABLES

Table 1. Method Analytes and Potential Interfering Elements

Analyte	Wavelength, nm	Plasma View	Potential Interfering Elements***
Al	308.215	Radial	Co, Mo, Ti, V
Sb	206.836	Axial	Ce, Cr, Fe, Mo, Ti, V
As	188.979*	Axial	Ce, Cr, Co, Mo, Ti
As	193.696****	Axial	Co, Mn, Mo, Ti, V
Ba	233.527*	Radial	Mo, V
Be	313.107*	Radial	Ce, Cr, Ti, V
B	249.677	Radial	Co, Fe, Mo, V
Cd	226.502	Axial	Fe, Ni, Ti
Ca	315.887	Radial	Cr
Ce	413.764	Radial	None
Cr	205.560	Axial	Ce, Be, Fe, Mo, Ni
Co	228.616	Axial	Ba, Cd, Cr,Ni, Ti
Cu	324.752	Radial	Fe, Mo
Fe	273.955*	Radial	Ti
Pb	220.353	Axial	Al, Ce, Co, Cu, Fe, Mo, Ni, Ti
Li	670.784	Axial**	None
Mg	279.077	Radial	Mn
Mn	260.568*	Radial	Co, Fe
Mo	202.031*	Axial	None
Ni	231.604	Axial	Co, Mo
K	766.490	Radial	None
Se	196.026	Axial	Ce, Al, Co, Fe, Mn, Mo, Ti, V
SiO_2	251.611	Radial	Mo
Ag	328.068	Axial	Ce, Cu, Fe, Mn, Ti, V
Na	589.592*	Radial	None
Sr	421.552	Radial	None
Tl	190.801*	Axial	Ce, Cr, Co, Fe,Mn, Ti, V
Sn	189.927*	Axial	Mg
Ti	334.940	Radial	Ca, Cr
V	292.402	Axial	Ce, Cr, Fe, Mn, Mo, Ti
Zn	213.857	Radial	Ca, Cu, Fe, Ni

Note: *Wavelengths other than those recommended by Method 200.7
**Axial view with high resolution

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***All potential interfering elements based on ½ QL interference level. Underlined potential interfering element often requires daily testing per Section 9.2.3.

****Additional arsenic line added to monitor possible calcium background interference.

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Table 2. Calibration Standard Concentrations*

Analyte	Solution	Concentration mg/L	Analyte	Solution	Concentration mg/L
As	Cal 5	10.0	Co	Cal 4	2.0
Ca	Cal 5	10.0	V	Cal 4	2.0
Sb	Cal 5	5.0	Al	Cal 3	10.0
Ba	Cal 5	1.0	Cr	Cal 3	5.0
B	Cal 5	2.0	SiO_2	Cal 3	10.0
Cd	Cal 5	2.0	Sn	Cal 3	4.0
Cu	Cal 5	2.0	Ti	Cal 3	10.0
Mn	Cal 5	2.0	Zn	Cal 3	5.0
Se	Cal 5	5.0	Be	Cal 2	1.0
Ag	Cal 5	0.5	Fe	Cal 2	10.0
K	Cal 6	20.0	Mg	Cal 2	10.0
Mo	Cal 6	10.0	Ni	Cal 2	2.0
Na	Cal 6	10.0	Pb	Cal 2	10.0
Sr	Cal 6	1.0	Tl	Cal 2	5.0
Ce	Cal 4	2.0	Li**	Cal 2	2.0

Note: *Mixes are prepared as needed from individual stock standards. Prepared mixed standards may also be purchased. All calibration sources are different than the source of the ICV/CCV/SCV.
**Lithium standard is from an individual stock and is used for Li method only.
***Cal 1 is the calibration blank.

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Table 3. ICV/CCV/SCV, LCS/MS/MSD Concentrations

Analyte	ICV/SCV/CCV mg/L	LCS/MS/MSD mg/L
Al	2.0	2.0
Sb	2.0	0.80
As	2.0	0.80
Ba	2.0	0.20
Be	2.0	0.20
B	2.0	0.30
Cd	2.0	0.20
Ca	2.0	1.0
Ce	2.0	2.0
Cr	2.0	0.40
Co	2.0	0.20
Cu	2.0	0.30
Fe	2.0	3.0
Pb	2.0	1.0
Li	0.5	0.20
Mg	2.0	2.0
Mn	2.0	0.20
Mo	2.0	0.40
Ni	2.0	0.50
K	10.0	10.0
Se	2.0	2.0
SiO_2	10.0	2.0
Ag	0.5	0.075
Na	2.0	3.0
Sr	2.0	0.20
Tl	2.0	2.0
Sn	2.0	0.70
Ti	2.0	0.20
V	2.0	0.30
Zn	2.0	0.20

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APPENDIX E.
TYPICAL INSTRUMENT PARAMETERS

Nebulizer Gas Flow setting:	0.40 - 0.60 L/min
Auxiliary Gas Flow setting:	0.2 L/min
Plasma gas Flow setting:	15 L/min
ICP RF Power setting:	1500 W
Argon Line Pressure:	>100 psi
Resolution Setting:	Normal
Resolution Setting, Li Method:	High
Replicates:	4
Read Parameters:	minimum 2 – 5 sec., maximum 10 – 20 sec.
Rinse Time:	120 – 240 sec., typical
Flush Time:	50 - 70 sec.

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APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Maintenance Schedule for the PE Optima 5300 DV

Item	Frequency	Comments
Auto-sampler Rinse Station Reservoir	As needed	Fill with 2% $HN0_3$ / 2% HCl
Pump Tubing	Daily	Check for fatigue and wear. Replace as needed.
Drain Tubing	Daily	Check for good drainage, adjust as needed
Nebulizer Spray	Daily	Check, unclog by back flushing if needed
Torch Tip	Daily	Check for sample residues. Replace with clean glassware if needed.
Argon Dewar	Daily	Check for sufficient amount and pressure. Order as needed.
Auto-sampler and Peristaltic Pump	Daily	Wipe spills or residues.
Glassware	Weekly or needed	If excessive carryover, inspect and clean if needed.
Radial and axial windows	Monthly or as needed	If sensitivities fall or cloudiness noted replace with clean windows.
Air filters	Monthly	Clean as needed.

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APPENDIX G.
DECISION TREE FOR REPORTING METALS

Aluminum (Al)	X		XXX
Antimony (Sb)	X		XXX
Arsenic (As)	X		XXX
Barium (Ba)	X		XXX
Beryllium (Be)	X	XX	
Boron (B)		XX	
Cadmium (Cd)	X		XXX
Calcium (Ca)		XX	
Chromium (Cr)	X		XXX
Cobalt (Co)	X		XXX
Copper (Cu)	X		XXX
Iron (Fe)		XX	
Lead (Pb)	X		XXX
Magnesium (Mg)		XX	
Lithium (Li)		XX	
Manganese (Mn)	X		XXX
Molybdenum (Mo)	X		XXX
Nickel (Ni)	X		XXX
Potassium (K)		XX	
Selenium (Se)	X		XXX
Silica (SiO_2)		XX	
Silver (Ag)	X		XXX
Sodium (Na)		XX	
Strontium (Sr)		XX	
Thallium (Tl)	X		XXX
Thorium (Th)	X		
Tin (Sn)		XX	
Titanium (Ti)		XX	
Uranium (U)	X		
Vanadium (V)	X		XXX
Zinc (Zn)	X		XXX

Where:

X = reported by ICP-MS

XX = reported by ICP-AES

XXX = if all 200.7 QC passes and the concentration is above the 200.7 QL, an element may be reported from the 200.7 analysis.

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APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 505
Revision: 9, Effective: 07/15/2015

DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-AES

Revision	Effective Date	Description
7	09/17/09	1. Minor revision to integrate LIMS into procedure and revise format to current SOP 850 requirements. 2. Section 7.3.8, added Be and removed Sn as an SIC solution. 3. Section 8.3.2, updated analytical sequence and added a note on when to analyze Be, Ce, and Cd SIC solutions. 4. Section 8.3.3 step 1, changed limit correction from 1/5 to 1/2 the QL. 5. Appendix A, replaced Be with Sn as a not analyzed SIC solution. 6. Appendix B, changed Li QL to 5 *u*g/L from 10. 7. Appendix D, Table 1: (1) Updated potential interfering elements to current instrument conditions, (2) Updated Be to radial view; Cd and Sn to axial view. 8. Appendix D, Table 2, changed Ce concentration to 2 mg/L and to Standard III. 9. Appendix G, updated decision tree. 10. Appendix D updated 3/1/2011 to change plasma view on Cr, Co, Mo, Ni and V to axial for improved sensitivity.
8	06/01/12	1. Section 3, update CB definition. 2. Section 7.3.8, update SIC solutions used. 3. Sections 9.2.3 and 9.2.9, clarify SIC check. 4. Appendix B, lowered QL limits for Be, Co, Li, Ag, Sr, and V. 5. Appendix D, update interfering elements table. 6. Miscellaneous edits throughout.
9	07/15/15	1. Updated MS/MSD frequency to be consistent with the rest of the laboratory. 2. Additional arsenic line (193.696 nm) added to monitor possible calcium background interference. 3. Added note about elements exceeding extremely hazardous waste concentrations to Section 4.4. 4. Miscellaneous edits throughout.

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